SOURCING COAL COMBUSTION-DERIVED PAH IN THE ENVIRONMENT

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ABSTRACT

To investigate the effects of domestic coal burning on the distribution and isotopic composition of environmental PAH, a series of soil samples were collected in a coal-burning village (Lochwinnoch) nearby Glasgow, UK. Analyses showed that, typically, PAHs in the Lochwinnoch samples were isotopically heavy having $\delta^{13}C$ values close to -25 ‰ that are consistent with the PAHs emanating from coal burning. It was also noted, however, that alkylated PAHs would appear to be more prominent in soot from coal fires than in the samples collected in Lochwinnoch where domestic combustion was determined to be the major source. Therefore, to address the possibility that parent PAHs may survive in soils preferentially, two weathering experiments have commenced using a low temperature coal carbonisation tar from the Coalite process. Initial results have shown that after as little as 80 days weathering period, parent PAHs, particularly fluoranthene and pyrene, become more prominent than the alkylated species, suggesting that parent PAHs survive oxidation/weathering to a greater extent than their alkylated counterparts.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) in the environment arise from a number of potential natural and anthropogenic sources, with major contributions from coal utilisation [1], diesel exhaust emissions [2] and biomass combustion – both accidental and intentional [3]. Although conventional analytical techniques are useful for the identification and quantification of PAH in environmental samples, they provide little information on the source of these pollutants. The potential of using compound-specific isotopic analysis for source-apportionment of environmental PAH has been demonstrated by O'Malley et al. [4,5], Lichtfouse et al. [6] and the authors [7-10]. O'Malley et al. indicated that PAH arising from woodburning and vehicle emissions exhibited significantly different isotopic signatures [4] and the same authors have also reported the isotopic compositions of n-alkanes and PAH produced from combustion of C3 and C4 plant species [5]. Lichtfouse et al. [6] have reported significant anthropogenic hydrocarbon inputs into soil using a combination of biomarker, $\delta^{13}C$ and ^{14}C analyses. The authors have found that the $^{13}C/^{12}C$ isotopic ratios for PAH derived from coal and wood pyrolysis and diesel particulates vary over a range of ca. 8 ‰ which could provide a basis for source apportionment in a number of environments [7].

To establish a basis for applying gas chromatography - isotope ratio mass spectrometry ($\delta^{13}C$ GC-IRMS) to source PAHs from coal utilisation, stable isotopic ratios have been determined as a function of coal rank and process conditions [8-10]. The results have indicated that the primary control on the isotopic values of coal-derived PAHs is the extent of ring growth required to form PAHs during processing. Thus, for relatively mild conversion processes such as low temperature carbonisation where the major aromatics are alkyl substituted 2-3 ring PAHs, the isotopic signatures are similar to those of the parent coals (ca. −25 ‰). However, the $\delta^{13}C$ values for the PAHs become lighter in going to high temperature carbonisation, gasification and fluidised-bed combustion as the extent of ring condensation increases and confirming that the PAHs are not released as primary volatiles. To demonstrate the applicability of the technique to the analysis of environmental PAHs where major inputs from coals could be expected, samples collected in the vicinity of a low temperature carbonisation plant in the UK were analysed [9,10]. .In addition to low temperature coal tar, significant inputs of PAHs from transport fuels, high temperature carbonisation and combustion sources (coal/biomass) were inferred from the isotopic ratios, taken in conjunction with the differences in alkyl substitution patterns.

In this paper we report findings on PAH formation in domestic (grate) combustion and resultant isotopic compositions. Furthermore, to trace PAH from domestic combustion, a series of soil samples have been collected in the area of Lochwinnoch, a village approximately 15 miles south west of Glasgow, UK, where a large proportion of the domestic properties still use coal combustion as a primary source of heating. To determine the fate of PAH following emission to the environment, an experiment has commenced using soil spiked with low

temperature coal carbonisation tar from the Coalite process [9,10] to investigate the effect of biodegradation/weathering on PAH survival and their resultant isotopic compositions.

EXPERIMENTAL

Three domestic soot samples were selected for analysis. The first sample (domestic fire soot 1) emanates from a single coal-burning fire chimney and the sample supplied by a local chimney sweep also comes from a series of fires burning only coal. However, the second soot sample (domestic fire soot 2) is from a domestic fire on which both coal and wood have been burned. Soil samples were collected from various points in the village of Lochwinnoch, 15 miles south west of Glasgow, UK. Collection sites encompassed areas the village Main Street (sample LW5), the centre of a residential area of the village (sample LW6) and a sample collected from a heritage trail approximately 1 mile from the centre of the village (sample LW7).

Soil from open ground approximately 1 mile from Glasgow city centre was dried at 40 °C *in vacuo*, and the soil sample was then mixed with a predetermined quantity of low temperature coal tar (20 % w/w). The coal tar-coated soil was divided into sub-fractions that were placed where the original soil sample was collected. Each sub- fraction was packed in a roughly cylindrical area to a depth of approximately 2 cm and diameter of 6 cm (the beds for each sub-fraction were approximately 3 cm apart). The sub-fractions have been recovered after increasing periods of time. By the time the second sample was taken (80 days), grass growth was already evident over the coal tar coated soil.

All soil and soot samples were dried *in vacuo* at 40°C, soil samples ground to 75-212 μm particle size and all samples (including tar pre-coated soil) extracted by reflux in dichloromethane (DCM) for 10 hours. The DCM extracts (following solvent removal) were fractionated by open column alumina chromatography (fine grain activated neutral alumina) to yield neutral aromatic fractions for δ^{13}C GC-IRMS analysis as described previously [7,8,10]. Reported isotopic data represent the arithmetic means of at least two duplicate analyses and the estimated repeatability for individual hydrocarbons, based on an earlier study by Eakin *et al* [11] with the VG Isochrom II GC-IRMS system, is 0.2-0.4 %. The experimental error of the machine was between 0.5 and 1.0 ‰, with precision decreasing as the intensity of GC peaks, in relation to the unresolved background, decreased.

RESULTS AND DISCUSSION

Domestic Soot Samples

Figure 1 compares the gas chromatograms for the neutral aromatics extracted from the domestic soot samples. The isotopic compositions of extracted PAH for 2 of the samples are listed in Table 1. The sample provided by the chimney sweep emanates from coal fires as does soot sample number 1 (collected from a single chimney). However, domestic soot sample number 2 was obtained from the chimney of a domestic fire on which both coal and wood have been burned. The parent PAHs in sample 2 are much more dominant than in the other two samples (Figure 1) and their δ^{13}C values are in the region of -28 to -30 ‰. As can be seen from Table 1, the isotopic compositions of PAH extracted from soot sample number 1, where coal is known to be the sole contributor, lie in the region of –25 ‰. Since UK bituminous coals are known to exhibit bulk isotopic compositions in the region of –24 to –25 ‰ [9,10], this would suggest that PAH released are primary volatiles from coal devolatilisation. By considering these isotopic compositions and also taking account of the fact that wood burning gives PAHs with values below -30 ‰ [7], it can be suggested that, in this instance, the PAHs in domestic soot sample number 2 have been sourced from both coal and wood. The parent PAHs are more dominant in the soot provided by the chimney sweep than in the first domestic sample analysed, but alkylated PAHs are still major constituents (Figure 1). Comparison of the two coal-burning chimney samples suggests that the ratio of alkylated to parent PAHs varies considerably in soot from domestic fires and is clearly going to reflect the average devolatilisation temperature. The authors are now conducting tests under controlled conditions on both bituminous coals and smokeless fuels to further examine this phenomenon.

Lochwinnoch Soil Samples

Figure 2 shows the gas chromatograms for the neutral aromatics extracted from the Lochwinnoch soil samples investigated and Table 2 lists the δ^{13}C values of selected PAHs and the neutral aromatic yields for each of the samples. A full suite of samples have been analysed by GC, but the 3 samples selected for GC-IRMS exemplify the variations found in composition. Sample LW5 was collected from the village Main Street and, as well as the parent PAH peaks, a broad unresolved hump is also evident in the chromatogram. This is characteristic of the highly complex distribution of heavily substituted alkyl aromatics found in diesel particulates [7,9,10]. The

sample collected from a residential street (LW7) displays a similar distribution of parent PAH as the main street sample, but the broad shoulder arising from heavily substituted alkyl aromatics is much less prominent in the chromatogram (Figure 2), suggesting a lower input from diesel particulate. A sample was also collected from a heritage trail situated approximately one mile from the centre of the village (LW 6), which displays a different distribution of parent PAH to the other two samples. As can be seen from Table 2, the total concentration of neutral aromatics in the heritage trail sample (0.02 %) was also significantly lower than corresponding concentrations in the residential street sample (0.08 %) and the main street sample (0.2 %).

The $\delta^{13}C$ values for the parent PAH are generally quite similar for samples LW5 and LW7 and mainly occur in the range –24 to –26 ‰, consistent with the PAHs arising from domestic coal burning. However, alkylated aromatics are much less prominent in the residential street sample (LW7) than the soot samples obtained thus far from coal fires (cf. Figures 1 and 2). The slightly heavier values (*ca.* –24 ‰) for the lower molecular mass PAH in the main street sample (LW5) could be indicative of biodegradation/weathering having occurred to a greater extent in relation to LW7. The distribution of parent PAHs in the Heritage Trail sample (LW6) is significantly different to that for the other two samples. Further, the higher molecular mass PAHs and phenanthrene/anthracene are isotopically light (–29 to –30.5 ‰) suggesting an input from sources other than coal and diesel. The location of the Heritage Trail sample in conjunction with the isotopically light PAH would suggest an input from biomass combustion.

Weathering experiment
The GC traces of the neutral aromatics from the initial low temperature tar and the tars recovered after the soil had been in the ground for 40 and 80 days are compared in Figure 3. After 40 days, the lower molecular mass constituents (alkylnaphthalenes) decreased to a considerable extent and, after 80 days, the proportions of parent PAHs remaining, notably fluoranthene and pyrene, are beginning to increase in relation to the complex distribution of alkylated aromatics whose peaks dominate the GC trace for the initial tar. Thus, these preliminary results appear to provide direct evidence that, even after a relatively short weathering period, the alkylated aromatics are beginning to be depleted preferentially in relation to the parent PAHs.

CONCLUSIONS

The PAHs in the Lochwinnoch village samples were isotopically heavy having $\delta^{13}C$ values close to -25 ‰ that are consistent with the PAHs emanating from coal burning. The sample collected from a trail outside the centre of the village exhibited a different distribution of PAH to those collected on the main street and residential area. However, alkylated PAHs appear to be more prominent in soot from coal fires than in the samples collected in Lochwinnoch where domestic combustion was determined to be the major source. Initial results from a weathering experiment show that after as little as 80 days, parent PAHs, particularly fluoranthene and pyrene, become more prominent than alkylated species, suggesting that these compounds may survive biodegradation to a greater extent than their alkylated counterparts.

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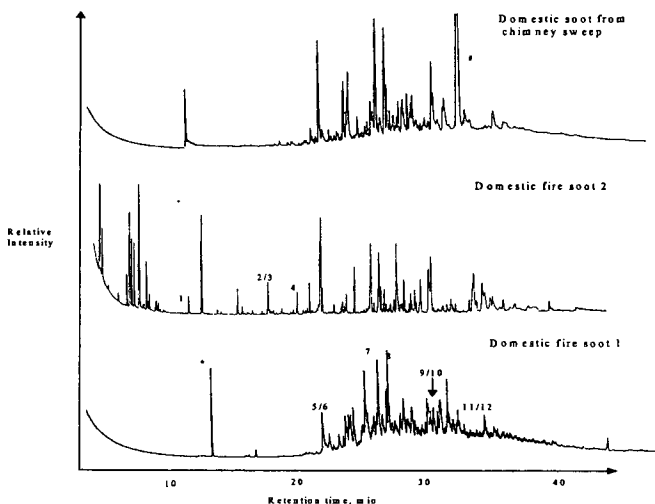
Figure1 GC traces for the aromatics from the domestic soot samples

Key 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene;8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; 14. Dibenz(a,h)anthracene;15. Benzo(ghi)perylene; 16. Indeno(1,2,3)pyrene; * Internal standard; #plasticiser
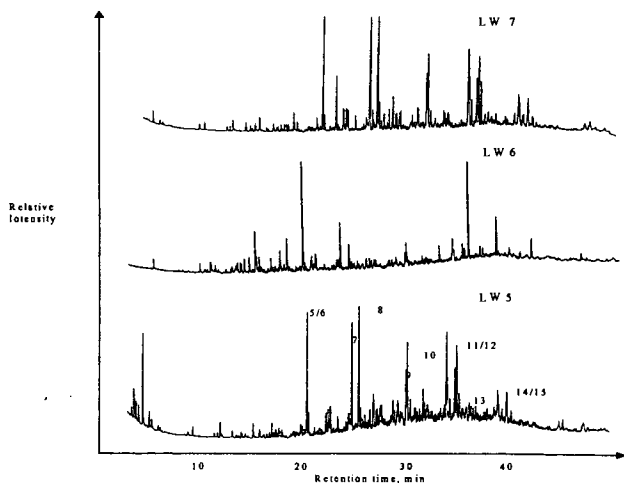

Figure 2 GC traces for aromatic fractions from Lochwinnoch samples

Key 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene ; 13. Benzo(a)pyrene; 14. Dibenz(a,h)anthracene; 15. Benzo(ghi)perylene; * Internal standard.

Table 1 Isotopic compositions of PAH extracted from domestic soot samples

PAH	Soot 1	Soot 2
Phenanthrene	-24.8	-29.0
Anthracene	-25.5	-28.9
Fluoranthene	-25.9	-30.6
Pyrene	-26.1	-28.9
Benzo(a)anthracene	-25.2	-29.5
Chrysene	-25.2	-29.4
Benzo(a)fluoranthene	-24.2	-29.4
Benzo(k)fluoranthene	-24.5	-29.5

Table 2 Neutral aromatic yields and isotopic compositions of PAH extracted from Lochwinnoch samples

| PAH	Sample/Isotopic Composition (‰)		
	LW 5	LW 6	LW 7
1. Naphthalene	-24.6	-	-
2. Acenaphthylene	-	-	-25.0
3. Acenaphthene	-	-	-25.0
4. Fluorene	-23.9	-25.1	-25.8
5. Phenanthrene	-23.7	-29.1	-25.6
6. Anthracene	-23.7	-29.1	-28.1
7. Fluoranthene	-24.7	-25.0	-25.1
8. Pyrene	-25.3	-25.2	-25.7
9. Benzo(a)anthracene	-24.7	-26.0	-26.0
10. Chrysene	-24.7	-26.0	-26.0
11. Benzo(a)fluoranthene	-25.2	-30.5	-25.7
12. Benzo(k)fluoranthene	-25.2	-30.5	-25.7
13. Benzo(a)pyrene	-25.3	-30.5	-26.8
Neutral aromatic yield (%)	0.21	0.02	0.08
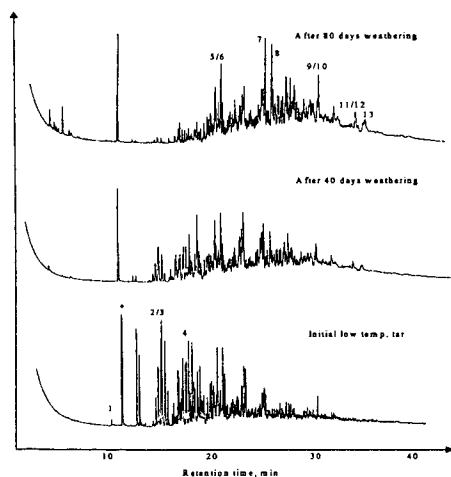
Figure 3 GC traces for aromatic fractions from the coal tar and soil extracts after 40 and 80 days
Key 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; *Internal Standard.